Auger-Electron Emission Resulting from the Annihilation of Core Electrons with Low-Energy Positrons

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We report the first demonstration of positron-induced Auger-electron spectroscopy. A beam of low-energy (10^1 eV) positrons was used to create core holes at the surface of Ni and Cu by matter-antimatter annihilation. Estimates are developed for the probability of positrons annihilating with a $3p$ electron found to be as high as $3.7(7)\times10^{-2}$ in Ni. The implications of the extremely high signal to background are discussed and several important advantages of this process for surface analysis are suggested.

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Although Auger electrons provide an extremely useful probe of the elemental composition of the first few atomic layers of the surface, serious limitations are imposed on conventional electron-excited Auger-electron spectroscopy (EAES) by the fact that an electron beam of sufficient energy to excite a core hole creates a background of backscattered and secondary electrons which is typically many times larger than the relatively weak Auger signal. The intense primary beam can cause damage to organic systems, charging problems in insulators, and desorption of adsorbed layers, thus limiting the utility of EAES for these systems. In addition, the energetic primary beam generates an excited volume deep below the surface (this is also true for x-ray excited Auger emission). Although the short escape depth of the Auger electrons provides surface selectivity, the signal still represents an average over several atomic layers.

In this paper we report on experiments that demonstrate a fundamentally new process for the excitation of Auger electrons in which low-energy positrons are used to remove core electrons by matter-antimatter annihilation and not by collisional ionization. In metals, the mechanism for low-energy positron-induced Auger-electron emission can be described as follows: Positrons implanted at low energies have a high probability of diffusing back to the surface and getting trapped in defects at or near the surface[1] or in a surface state.[2] A fraction of the trapped positrons will then annihilate with a core electron creating a core hole excitation which can then relax via the familiar Auger process (see Fig. 1). Because of the use of low incident beam energies and the elimination of problems of beam damage and large background (energy conservation forbids the production of collisionally excited secondaries with energies larger than the incident beam energy) the observed mechanism may make feasible a new surface analytic technique: Positron-annihilation–induced Auger-electron spectroscopy (PAES).

Measurements were performed first at the Brookhaven National Laboratory on a Ni(110) surface utilizing an electrostatically focused positron beam described previously.[3] Energy analysis and single electron counting were performed with a retarding field analyzer comprised of a microchannel plate (MCP) equipped with standard four-grid LEED optics. The sample was maintained at -2.6 V to attract low-energy positrons reemitted from the surface back to the sample. The sample was cleaned *in situ* and annealed at 750 °C. LEED and retarding field EAES indicated approximately 13% of an ordered S overlayer. Other impurities including carbon and oxygen remained below detectable limits. Positrons were incident on the sample with a kinetic energy of 42 eV.

The integral energy spectrum of electrons leaving the Ni(110) sample resulting from positrons incident at 42 eV is shown in Fig. 2. A "beam off" background due almost entirely to detector dark counts had been subtracted. The striking feature of this figure is that electrons are observed at energies greater than the incident posi-

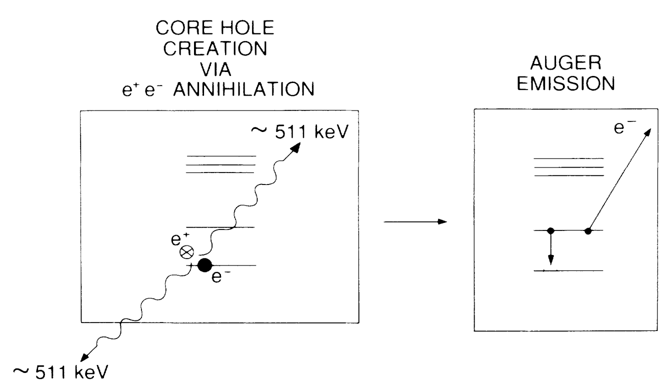

FIG. 1. Energy level diagram indicating the process of positron-annihilation–induced Auger-electron emission. A core hole is created by the annihilation of a core electron with a positron. This is followed by Auger-electron emission.

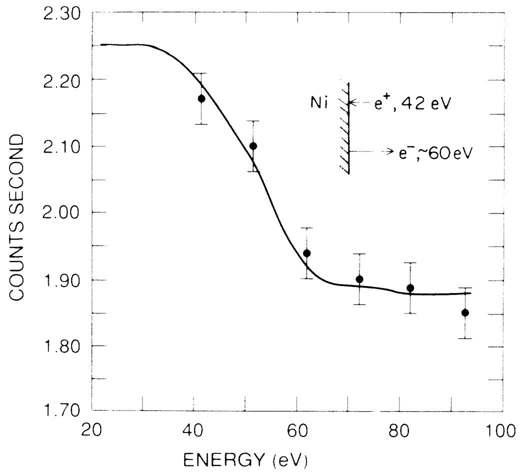

FIG. 2. Integral energy distribution of electrons leaving Ni(110) (S) surface under bombardment by 42.6-eV positrons. The solid line is a fit to a function consisting of a numerical integration of the Ni $M_{23}M_{45}M_{45}$ line (measured with an electron beam) plus a constant background.

trons. We argue that these electrons can only be due to Auger electrons resulting from annihilation-induced core holes. Excitation of core holes by positron-electron collisions can be ruled out since the 42-eV energy with which the incident beam hits the sample is less than the 75 (73) eV necessary to ionize the M_2 (M_3) core levels. Direct collisional excitation of secondary electrons with energies greater than 42 eV is also forbidden by energy conservation. Other indirect processes in which annihilation γ rays produce energetic electrons via Compton scattering or photoemission could lead to the generation of Auger electrons or a secondary electron background. Coincidence measurements, which are discussed later, indicate that the contribution due to these processes is less than 1% of the observed e^- emission rate.

The solid line shown in Fig. 2 is the result of a fit to a function obtained from numerical integration of the electron energy distribution of the Ni $M_{23}M_{45}M_{45}$ Auger transition measured by Allenspach *et al.*[4] using conventional electron beam techniques. Only an overall normalization and a constant background (neither of which affect the shape of the curve) were used as adjustable parameters in the fit. The number of Auger electrons per incident positron emitted into the solid angle subtended by the detector per incident positron $[A(\Omega)]$ was determined from the scale factor to be $A(\Omega)=1.0(2)\times10^{-3}\,e^-/e^+$.

In view of the potential significance of the Ni results, the measurements were repeated on a different sample and on a different apparatus as a stringent test of the reproducibility of the phenomena. These measurements were performed at the University of Texas at Arlington on Cu using a magnetically guided positron beam and a detector system[5] similar to the apparatus reported by Gullikson *et al.*[6] A trochoidal energy spectrometer equipped with a 25-mm-diam microchannel plate was used to energy analyze and detect electrons emitted from the sample. A Nd-Fe-B magnet was placed behind the sample to reduce the angular spread of the Auger electrons at the spectrometer.[6] A NaI(Tl) detector was used to measure annihilation γ rays emitted in coincidence with the Auger electrons. The sample was cleaned by ion bombardment prior to the measurement. Previous use of this cleaning procedure in our system produced a Cu surface that maintained carbon and oxygen contamination levels below 10% for a period corresponding to the time period of our measurements.

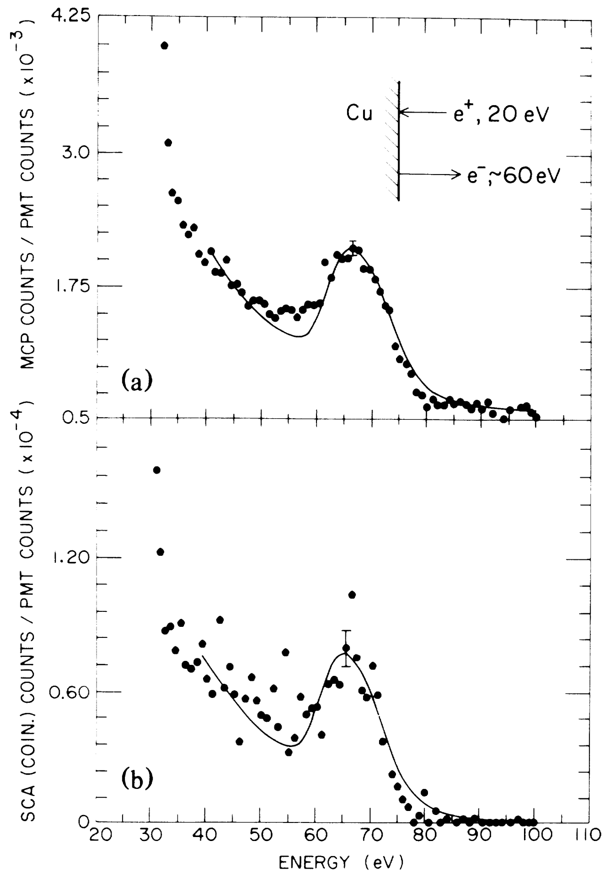

FIG. 3. The energy spectra of electrons leaving the polycrystalline copper surface under bombardment by 20-eV positrons. The signal plotted in (a) is obtained directly from the MCP detector. (b) The same spectrum but with the signal obtained from the detection of electrons in coincidence with annihilation γ rays from the sample. The background due to accidental coincidence is 1.2×10^{-6} count/photomultiplier tube count. The sample was biased at -10 V with respect to ground (the reference of the energy spectrometer). The peak at 65 eV corresponds to the $M_{23}M_{45}M_{45}$ Auger transition. The solid line represents a fit to a function obtained by our convoluting the energy distribution for the 60-eV (nominal) $M_{23}M_{45}M_{45}$ Auger transition for Cu measured by EAES with the instrument response function.

A typical energy spectra of electrons leaving the copper surface are shown in Fig. 3. The signal plotted in Fig. 3(a) is obtained directly from the MCP detector. Figure 3(b) shows the same spectrum but with the signal obtained from the detection of electrons in coincidence with annihilation γ rays resulting from the removal of core electrons. The positrons were incident on the surface with a kinetic energy of 20 eV. The sample was biased at -10 V with respect to ground (the reference of the energy spectrometer) and the ratio of the magnetic field at the spectrometer to that at the sample,[6] B_0/B_1, was 0.17. The peak at ~ 65 eV corresponds to the $M_{23}M_{45}M_{45}$ Auger transition. The solid curves shown in Fig. 3 represent a fit to a function obtained by our convoluting the instrumental response function for our spectrometer (if we assume that the electrons leave the surface with an isotropic angular distribution) with the energy distribution for the 60-eV (nominal) $M_{23}M_{45}M_{45}$ Auger transition for Cu taken from EAES measurements of Zehner, Noonan, and Maden.[7] The amplitude of the resulting function was scaled from a one-parameter least-squares fit to the data from which an exponentially decreasing "background" had been subtracted. The function is shown plotted on top of the exponential. The width of the peak and the centroid position came directly from our instrumental response function and the previous EAES measurement and were not adjustable parameters. Integrating under the peak in the spectrum shown in Fig. 3(a) we obtain [taking into account the NaI(Tl) and the MCP efficiencies], $A(\Omega) = 9.8(4)\times 10^{-4}$ $M_{23}M_{45}M_{45}$ Auger electrons emitted from the sample per incident positron.

A number of tests were applied to make sure that the signal was due to positron-induced Auger electrons. The Auger peak disappeared and the coincidence signal dropped to the accidental rate when the sample was biased at 30 V to prevent the 10-eV positrons from hitting the sample. Evidence that the signal originated from the surface of the sample can be seen in the fact that the Cu signal was observed to have decreased by a factor of 2 because of surface contamination resulting from exposure to a pressure in the 10^{-10}-Torr range for a period of two days. The signal returned to its original level after ion bombardment. The 65-eV peak in the coincidence spectrum [Fig. 3(b)] confirms our description of the new mechanism by demonstrating the correlation between the Auger electrons and the annihilation process. The copper measurements were repeated[8] with -5, -10, and -15 V on the sample; with incident positron energies of 15, 20, and 25 eV; and with $B_0/B_1 = 0.17$ and $B_0/B_1 = 0.32$. In each case the peak position and width were correctly predicted by simply our convoluting the calculated instrumental response function with the EAES data of Zehner, Noonan, and Maden.[7] The fact that our calculation matched the peak position and width with no adjustable parameters is strong evidence that we are seeing positron-induced Auger emission. Further evidence comes from the fact that the measured signals were consistent with upper bounds predicted from theoretical estimates.

In order to compare the observed and theoretical signal strengths, we estimate $\sigma(M_{23})$, the probability that a positron trapped at the surface will result in the annihilation of electrons in the M_2 or M_3 level, from our results using Eq. (1):

$$\sigma(M_{23}) = A(\Omega)(4\pi/\Omega)(1/f_s)(1/b)(1/SM_{23}), \quad (1)$$

where $A(\Omega)$ is defined above; $4\pi/\Omega$ takes into account the solid angle of the detector; f_s is the fraction of incident positrons that get trapped at the surface; b is the fraction of Auger electrons (resulting from annihilations of positrons) that escape into the solid angle, Ω, without suffering significant energy loss; and SM_{23} is the probability that an M_{23} core hole results in a $M_{23}M_{45}M_{45}$ Auger transition. The solid angle term $\Omega/4\pi$ for the MCP is 0.06. Theoretical calculations indicate that SM_{23} is nearly unity.[9] We estimate f_s to be 0.5 from the positronium thermal desorption measurement of Rosenberg, Weiss, and Canter[10] for a Ni(100) surface and the assumption that all the reemitted positrons are attracted back to the surface. For the purpose of obtaining an estimate of the transmission factor b, we will assume that the positron is bound in a surface state which implies that the probability density of the positron dies off quickly as a function of the depth and that the vast majority of annihilations with core electrons are with atoms in the first layer. Assuming the form, $b \simeq \exp(-t/\lambda)$, and taking $t = 0.6$ Å (half the distance between atomic planes), and $\lambda = 4$ Å the measured value for the escape depth for the 61-eV Ni Auger electron,[11] we get $b = 0.86$ (if the positrons are not trapped in a surface state but rather in some other near-surface trap, the transmission factor will be smaller). Inserting these values into Eq. (1) we calculate that $\sigma(M_{23}) = 3.7(7)\times 10^{-2}$. Performing a similar calculation for Cu, we find that $\sigma(M_{23}) = 0.46(2)\times 10^{-2}$ (the errors quoted in all cases account for counting statistics only). For Cu we use the same values for b and f_s as for Ni and take $\Omega = 2\pi$. As expected, the values of $\sigma(M_{23})$ are similar for the two metals. The lower value of $\sigma(M_{23})$ for Cu may be due in part to increased subsurface trapping of positrons in the unannealed, polycrystalline Cu sample.

These estimates of $\sigma(M_{23})$ are within an order of magnitude of the theoretical estimate of $\sigma(M_{23}) = 7\times 10^{-2}$ for Ni obtained from the calculations of Niemenen and Jensen of the fraction of positrons trapped in a Ni surface state that annihilate with core electrons[12] (although they did not calculate the individual contribution of the $3p$ levels, such calculations performed by Bonderup, Anderson, and Lowy[13] for bulk Cu indicate that 95% of annihilations with core electrons are with the $3p$ levels). Our values of $\sigma(M_{23})$ are also consistent with an upper bound of 6×10^{-2} which can be placed on the value for $\sigma(M_{23})$ in Cu from the calculations of the annihilation of positrons with $3p$ electrons in bulk Cu.[13] The fact that the values of $\sigma(M_{23})$ estimated from our measurements are lower than the theoretical values possibly reflects our overestimation of b because we did not take into account subsurface defect trapping or the effect of surface impurities. Future experiments, including thermal desorption measurement studies of annealed and roughened surfaces will examine the affects of defects and overlayers as well as the degree of surface specificity that is possible with PAES in systems in which positrons can become trapped in a surface state (metals and semiconductors).

The coincidence measurements shown in Fig. 3(b) indicate that there is almost no background on the high-energy side of the peak. The "background" on the low-energy side of the peak is due to Auger electrons that have lost energy on the way out of the sample and Auger electrons with large transverse components of momentum. This clearly demonstrates the ability of PAES to eliminate the secondary electron background which plagues EAES as well as the fact that the γ-ray-induced secondaries are a negligible contribution to the signal. Using an analysis similar to that used by Joshi, Davis, and Palmberg,[14] the signal strength, and the signal-to-background ratio obtained from Fig. 3(b), we find that PAES data can be obtained with 0.03 times the total charge dose as EAES with the same signal-to-noise ratio. This thirtyfold reduction in charge dose combined with a 2-order-of-magnitude reduction in beam energy, would result in a reduction in the total energy dose to the surface of more than 3 orders of magnitude with PAES as compared to EAES. The implementation of PAES by use of intense positron beam[15] of 10^7 positrons/sec which have recently become available (compared with the 10^4 positrons/sec in our Cu experiment) should enable Auger analysis to be performed on fragile adsorbed layers, chemically unstable systems, and insulators, where conventional electron excitation methods cannot be used because of beam damage or charging problems.

We have reported the first measurement of Auger-electron emission resulting from the annihilation of low-energy positrons with core electrons. The use of a positron beam energy less than the energy of the Auger electrons has enabled us to eliminate the large secondary electron background associated with conventional EAES. The measured PAES cross sections are large enough to provide useful Auger signals with existing positron beam technology.

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